

MULTIPHASE MATERIALS WITH LIGNIN. VI. EFFECT OF CELLULOSE DERIVATIVE STRUCTURE ON BLEND MORPHOLOGY WITH LIGNIN

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ABSTRACT

Polymeric blends of lignin with ethyl cellulose (EC) and cellulose acetate/butyrate (CAB) were prepared by solution casting from dioxane. Fracture surface analysis by scanning electron microscopy revealed phase separation when the lignin content exceeded 10% for blends with EC and 5% in the CAB system. While this phase behavior is as predicted for the EC blends, a greater level of compatibility had been expected for the CAB blend system. Results from both differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) suggest that the observed phase separation may be a consequence of supermolecular structure development rather than immiscibility. In the case of the EC/lignin blends, the observed T_g of lignin was 25 C and 35 C higher than that of the pure component for the 40 and 50 wt.% blend, respectively; and CAB/lignin blends produced conflicting results by DSC and DMTA. Where DSC revealed single T_g 's for all blends with up to approximately 20% lignin, and dual transitions for all other compositions, DMTA data reflected single relaxations with variable T_g 's throughout. This discrepancy is tentatively explained through the formation of liquid crystal mesophases in the cellulose derivative/lignin blends during solvent evaporation.

Keywords: Polymer blends, lignin, cellulose derivatives, phase behavior, glass transition temperature.

INTRODUCTION

The phenomenon of liquid crystal formation in polyesters has been used to develop high-modulus, high-strength materials of considerable commercial interest (Ciferri 1975). Cellulose (Chanzy et al. 1980) and a number of its derivatives (Jenkins and Stannett 1983; Nishio and Takahashi 1984) display similar behavior, but potential commercial exploitation of cellulosic liquid crystals has been directed toward the unique optical properties resulting from the cholesteric mesophase formed by these lyotropic systems (Tseng et al. 1981). Although considerable promise has been demonstrated with liquid crystal polyesters in binary blends (Paci et al. 1987; Joseph et al. 1985), only a few reports on polymer blends with cellulose derivatives are found in the literature (Hubbell and Cooper 1977; Cabbasso et al. 1974; Tamura et al. 1981). Recent studies on the phase morphology in blends of hydroxypropyl cellulose (HPC) with lignin and chemically modified lignin have shown that the level of miscibility greatly influences the development and retention of supermolecular structure in the blend (Rials 1986a). Increases in both tensile modulus and tensile strength of up to 150% were found for injection molded samples at low lignin contents (<20%). The lignin component was found to reinforce the amorphous cellulose derivative matrix in which an oriented liquid

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crystal mesophase structure is embedded. By analogy, this blend morphology is similar to that of conventional fiber-reinforced composites.

The presence of secondary interactions between blend components greatly enhances their miscibility, and subsequently the blend morphology (Coleman and Painter 1984). Hydrogen bonding is suspected to play a role in cellulose {derivative}/lignin {derivative} blends. In a previous study, this concern was addressed by incrementally removing hydroxy functionality from lignin through (partial) ethylation, acetylation, and propoxylation (Rials 1986b). The results indicated that intermolecular interactions do not substantially influence component miscibility. A considerable influence on the morphology of the blend system was, however, exerted by different lignin modifications, presumably by altering the conformational stability of lignin (created by a network of intramolecular hydrogen bonds). This study deals with the second alternative, in which the sensitivity to interaction of cellulose {derivative}/lignin {derivative} blends was investigated by manipulating the chemistry of the cellulose component. Cellulose derivatives were selected in which the original hydroxy functionality was replaced (in part) by ethyl ether and acetate/butyrate ester groups, providing different functional groups for hydrogen bonding with lignin.

EXPERIMENTAL

Materials

An (unmodified) organosolv lignin (L) from aspen wood was supplied by Biological Energy Corp. of Valley Forge, PA. Its molecular weight (polystyrene equivalent by GPC), $\langle M_n \rangle$ was 800 g/mol with a polydispersity of 3.4. Other features of this lignin have been described elsewhere (Muller and Glasser 1983). Ethyl cellulose (EC), with a reported ethoxy content of 50.5% (T150), was supplied by Hercules, Inc. Cellulose acetate/butyrate (CAB) was obtained from Tennessee-Eastman Co., Kingsport, TN.

Blend preparation

Individual component solutions (ca. 10 wt.%) were prepared in dioxane, and these were mixed by stirring for 12 hours. The blended solutions were cast into Teflon molds, where the solvent was allowed to evaporate at ambient conditions for 24 hours. The resulting films were removed from the molds, and transferred to a vacuum oven at 60 C for 1 week to remove residual solvent. The dried films were stored over P_2O_5 in a vacuum desiccator until testing.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC4 interfaced to the Thermal Analysis Data Station (TADS) was used for thermal analysis. Samples (ca. 20 mg) were scanned at a heating rate of 20 deg/min under a purge of dry nitrogen. The glass transition (T_g) was defined as one-half the total change in heat capacity ($1/2\Delta C_p$) associated with the transition. The melting temperature (T_m) was taken as the peak maximum unless otherwise noted.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical properties (Log E' and $\tan \delta$) were evaluated with a Polymer Laboratories, Inc. DMTA interfaced to a Hewlett-Packard 9816 microcom-

TABLE 1. Glass transition temperature (T_g) and melting parameters (T_m , ΔH_m) for ethyl cellulose (EC) blends with lignin (L) determined by DSC.

Lignin content (wt%)	T_g (EC) (°C)	T_g (L) (°C)	T_m (°C)	ΔH_m (cal/g ¹)
0	120	+	252	3.01
5	117	+	253	2.93 (2.85) ²
10	107	+	252	2.66 (2.71)
15	107	+	252	2.72 (2.56)
20	105	+	252	2.42 (2.41)
30	94	147	251	2.61 (2.11)
40	92	129	— ³	— ²
55	+	111	—	—
70	+	102	—	—
80	+	100	—	—
90	+	97	—	—
100	+	95	—	—

¹ Transition not present.² The values of ΔH_m have been corrected for the actual weight fraction of EC in the blend. Experimental values are given in parentheses.³ The melt parameters could not be accurately determined due to the reduced weight fraction of EC. No crystallinity could be detected for the 70% and higher blends.

puter. All samples were scanned at a heating rate of 4 deg/min and a frequency of 10 Hz. A single cantilever beam geometry was utilized on samples with typical dimensions of 1 mm \times 15 mm \times 0.25 mm (1 \times w \times t).

Scanning electron microscopy (SEM)

Fracture surfaces were prepared by immersing the materials in liquid nitrogen for about 1 minute and breaking. The samples were coated with carbon and a gold-palladium alloy. An Amray scanning electron microscope, Model AMR-900, was used for analysis.

RESULTS AND DISCUSSION

Ethyl cellulose (EC) blends

Results obtained by DSC with EC/L blend materials (Table 1) reveal single T_g 's up to a lignin content of 20%, which shift by about 15 C to lower temperature. Distinct phase separation, manifested by an additional transition, is detected only for lignin contents of 30% and 40%. The lower temperature transition arises, presumably, from the lignin component, while the higher T_g is attributed to EC. Both T_g values vary in relation to composition, with the lignin T_g being 35 C to 50 C higher than that of the pure material, and the T_g of EC diminishing by nearly 30 C as lignin content rises to 40%. This pattern of T_g variation may be explained either by: (a) the partial solubility of lignin in EC, with the low molecular weight fractions plasticizing the cellulose component, and the high molecular weight fractions experiencing T_g elevation in accordance with conventional relationships; or (b) through the formation of a separate phase from the amorphous component which has some superstructural organization of its own. A window of complete miscibility, or homogeneity, is indicated at the extremes of blend composition.

An evaluation of the melting behavior fails to indicate a substantial decrease in T_m ; and the observed decrease in the heat of melting, ΔH_m , does not substantially exceed that expected merely as a result of the diminished weight fraction of the crystallizable EC component in the blend. This necessarily leads to the conclusion



FIG. 1. Scanning electron micrographs of freeze-fracture surfaces of EC/L blends at compositions of: A) 95/5, B) 85/15, and C) 70/30. (Mag. = 2,000 \times)

that miscibility between the blend components is limited since any interaction between the two would be reflected through a depression of the melting temperature.

The evaluation of blend morphology by SEM supports much greater immiscibility, or material heterogeneity, than that indicated by DSC. While there is no phase separation indicated at a lignin content of 5% (Fig. 1A) globular domains become visible at 15% (Fig. 1B). As the lignin component in the blend is increased further, the extent of phase separation increases and changes in appearance. Whereas the rounded structures of the 15%-blend remain intact upon fracture, the discontinuous phase of the 30%-blend appears to have experienced brittle fracture such that these structures appear more rod-like as a phase inversion point is approached (Fig. 1C). From a purely qualitative viewpoint, the relative area of these inclusions appears to occupy more than 30% of the surface, raising further questions regarding the composition and exact nature of this morphological structure.

The dynamic mechanical properties of several EC/L blends (Fig. 2) produce agreement with SEM observations. Two distinct relaxations are revealed in the $\tan \delta$ spectrum at all blend compositions. With a lignin content of only 10%, a small shoulder is seen at 165 C, which is not present in the spectrum of pure EC. The position of this transition decreases in temperature by about 25 C as the lignin content rises to 40%. The peak related to EC is concurrently shifted to a lower temperature. These results agree, to an extent, with the observations made by DSC (Table 1) in which the observed relaxations occurred at temperatures considerably higher (for the lignin component) and lower (for EC) than would be expected for the respective pure components. Since it is difficult to attribute this observation to phase composition alone (i.e., partial miscibility), a more plausible explanation may lie in the formation of a supermolecularly ordered, discrete phase. The increasing solution concentration as a consequence of solvent evaporation may lead to a liquid crystal mesophase residue (the exact composition of which is, as yet, unknown) possessing greater order than an equivalent amorphous phase.

The concept of molecular organization finds support in the increase in modulus ($\log E'$) found at about 135 C (for pure EC, and declining to 126 C with lignin content rising to 40%) of the DMTA spectra (Fig. 2). It is this feature that is reflected in the prominent peak at the corresponding temperature in the loss tangent curve. Similar behavior has been observed previously for several other cellulose derivatives (Rials unpubl. data), and has been attributed to strain-in-

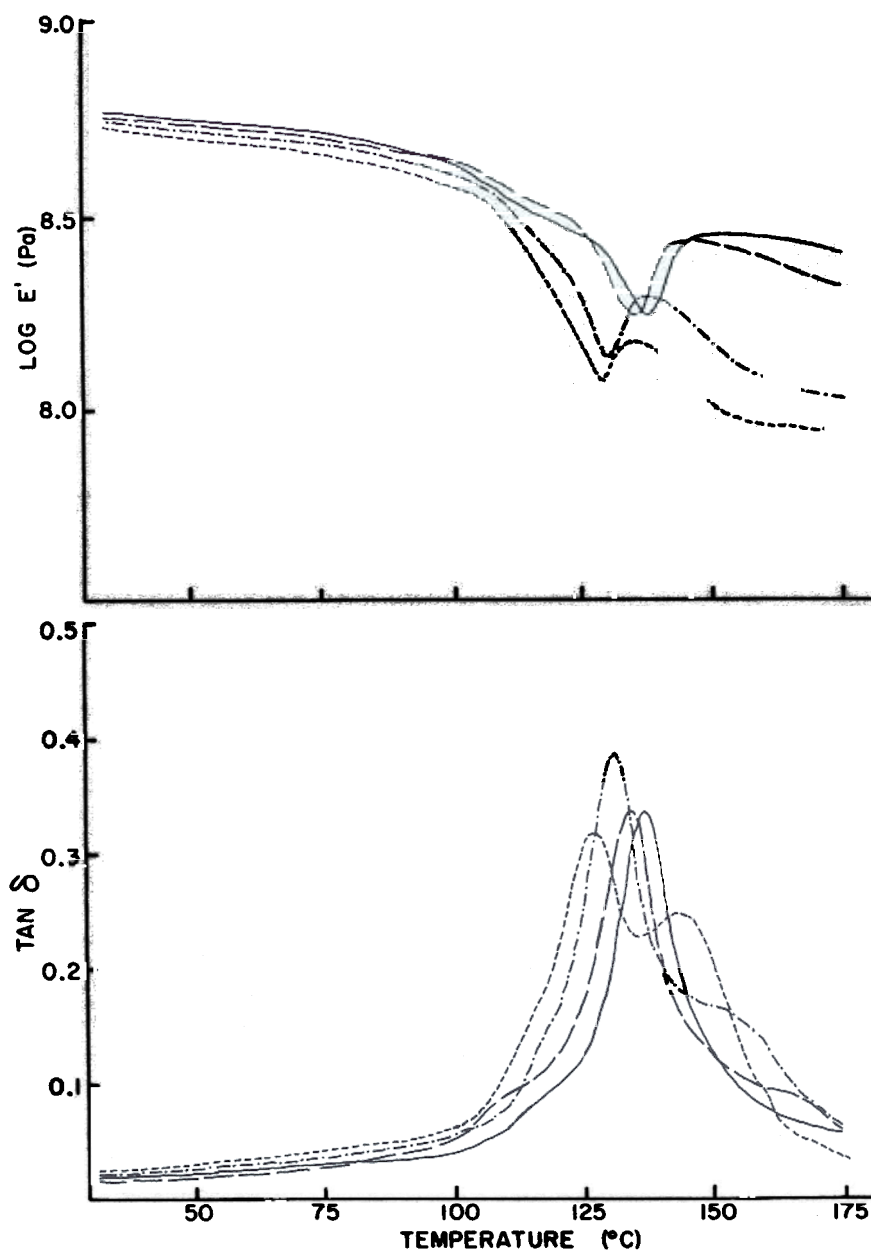


FIG. 2. Variation in dynamic mechanical properties ($\text{Log } E'$ and $\text{tan } \delta$) with temperature for blends of ethyl cellulose and lignin (EC/L): 100/0 (—), 90/10 (---), 80/20 (- · -), and 60/40 (···).

duced crystallization. When the materials are re-scanned through this temperature region (Fig. 3), no modulus increase is observed, which is consistent with this explanation. Re-scanning also results in reduced damping at 130°C (note difference of $\text{tan } \delta$ scale between Fig. 2 and Fig. 3), with the repeat $\text{tan } \delta$ maximum being more in line with the T_g of pure, amorphous EC. This provides additional evidence

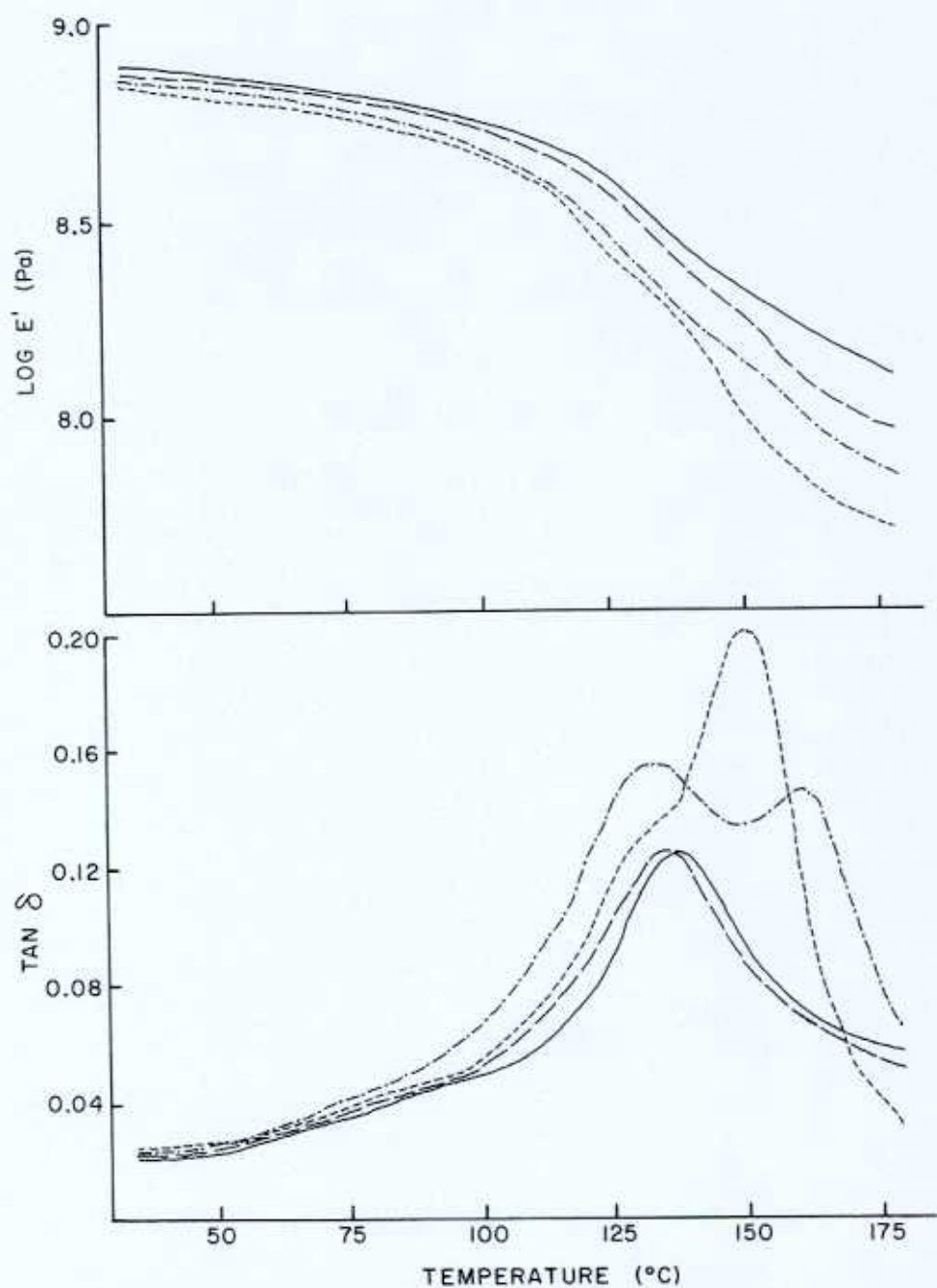


FIG. 3. Second scan of EC/L blends shown in Fig. 2: 100/0 (—), 90/10 (---), 80/20 (-·-·-), and 60/40 (·····).

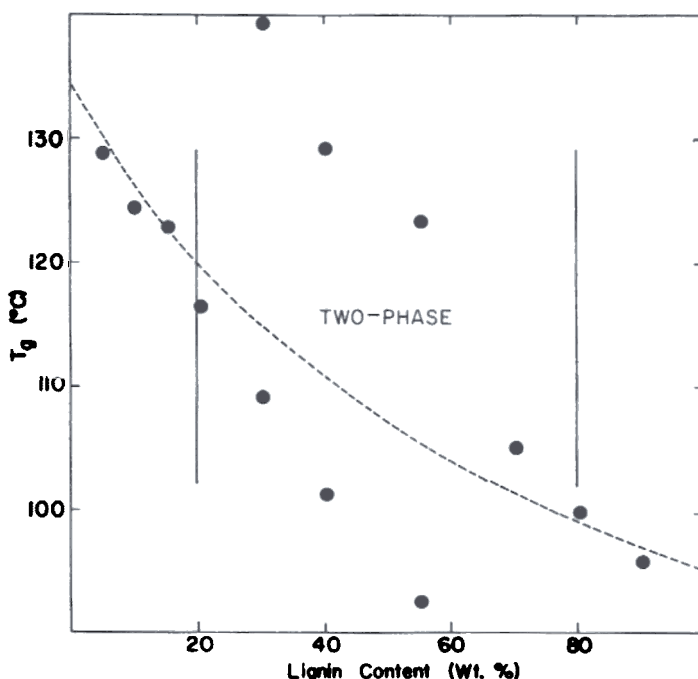


FIG. 4. Effect of blend composition on T_g behavior as observed by DSC of CAB/L blends. The dashed line is the predicted behavior from the Gordon-Taylor model (ref. 15).

in favor of supermolecular organization within the amorphous phase of EC/L blends.

Cellulose acetate/butyrate (CAB) blends

Miscibility enhancement in blends of lignin and hemicellulose has been attributed to acetylation, and thus the introduction of carbonyl functionality, by Erins et al. (1976). The interaction-promoting feature of C=O groups seems indeed supported (Fig. 4), although not to a significant extent. Two T_g 's are found in blends that contain between 20% and 80% lignin content, while a single transition is present at the extremes of blend composition. The latter is adequately modeled by the Gordon-Taylor equation (1952) using a value for the adjustable parameter, 'k', of 0.46. This (DSC) analysis suggests that the range of blend compositions producing a homogeneous system is slightly greater with CAB/L than with EC/L materials. Interestingly, within the two-phase region, there is a composition dependent variation in the two transition temperatures; however, the trend is again in contrast to that expected simply by considering possible differences in phase composition. Were this the case, a convergence of the two transitions would be encountered, rather than the observed parallel dependence.

Results by DMTA (Table 2) agree with this interpretation insofar as blend heterogeneity is indicated by the increased $\tan \delta$ peak width, which nearly doubles in relation to lignin content. The $\tan \delta$ peak fails to clearly reflect the presence of a two-phase morphology. Instead, a single $\tan \delta$ peak is found that exhibits a monotonic decrease from 143 C to 125 C as lignin content increases to 55%,



FIG. 5. Scanning electron micrographs of freeze-fracture surfaces of CAB/L blends at compositions of: A) 95/5, B) 85/15, and C) 70/30. (Mag. = 2,000 \times)

representing the maximum lignin composition yielding a testable film. This may simply be the result of a lack of physical integrity of the material after passing through the initial relaxation, making the second transition (as observed by DSC) inaccessible.

Fracture surface analysis by SEM again provides a somewhat contradictory view to this interpretation (Fig. 5). Phase separation into spherical domains embedded in a continuous matrix is evident even in the blends with the lowest lignin content. A considerable increase in domain size occurs as the amount of lignin increases to 15%, while very little change is found at 30%. Poor adhesion between dispersed phase and matrix resembles classical phase separation in an immiscible system.

Theoretical considerations

Since the heat of mixing provides an approximate measure of the free energy of mixing, it is generally indicative of the level of miscibility between two polymers. The heat of mixing for binary blends has been estimated by Schneier (1973), through Eq. 1.

$$\Delta H_m = \{ \chi_1 M_1 (\delta_1 - \delta_2)^2 / [(1 - \chi_2) M_2 \rho_2 + (1 - \chi_1) M_1 \rho_1] \}^2 \}^{1/2} \quad (1)$$

where χ , ρ , and M are the weight fraction of polymer, polymer density, and the monomer unit weight, respectively; and δ is the solubility parameter of components 1 and 2 as denoted by the subscripts. Although this approach is most generally applicable to non-polar blends, it has been successfully applied to blends of polar polymers where secondary interactions are not dominant (Singh and

TABLE 2. Results from dynamic mechanical analysis of selected cellulose acetate/butyrate blends with lignin.

Lignin content (wt%)	$\tan \delta$ T_{peak} ($^{\circ}$ C)	$\tan \delta$ PWHM ¹ ($^{\circ}$ C)
0	143	11.6
10	138	13.2
20	134	14.7
40	128	17.9
55	125	22.2

¹ Peak width at half-maximum.

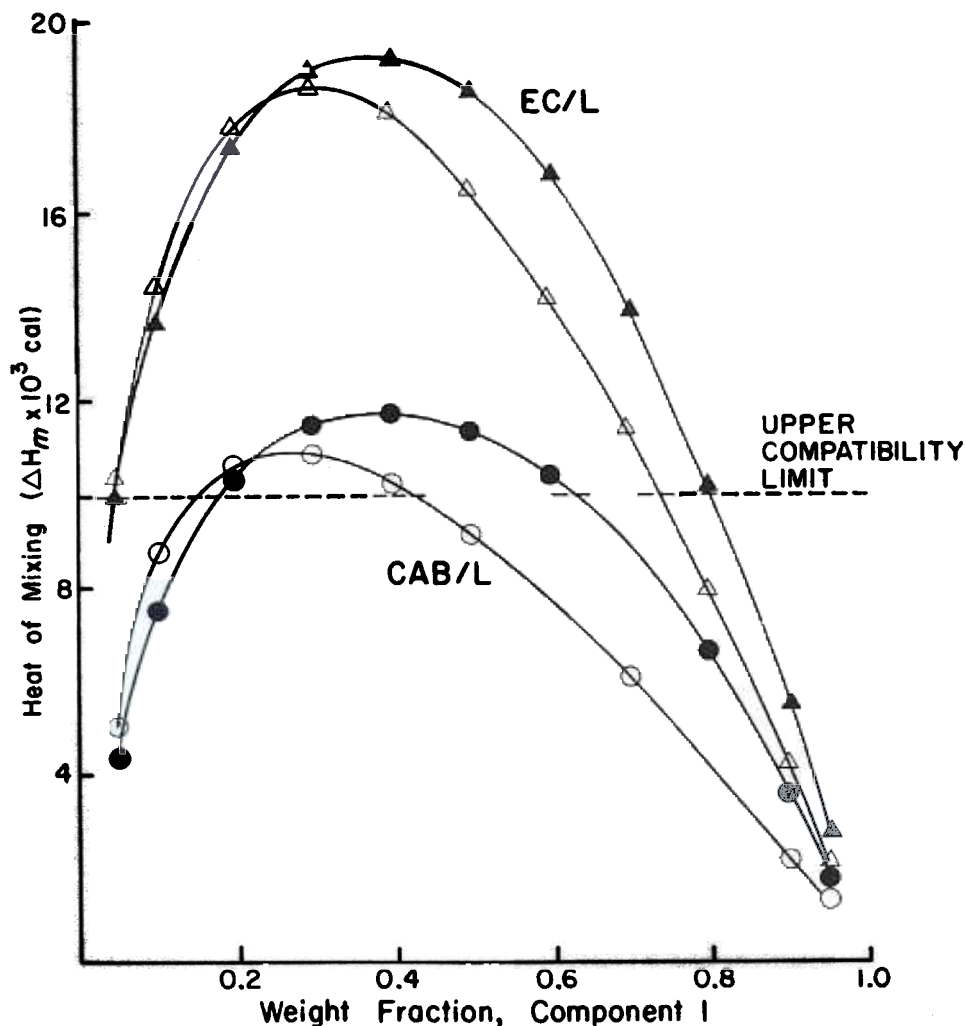


FIG. 6. Relationship between heat of mixing and weight fraction of component 1 in EC/L (Δ) and CAB/L (O) blends. The clear point markers result from calculation using lignin as component 1, and the solid point markers use the cellulose derivative as component 1.

Singh 1983). Since blends of both EC and CAB with lignin have proven to be largely heterogeneous, secondary interactions must contribute only minimally and Eq. 1 may be applicable. Pertinent values for the parameters of Eq. 1 are given in Table 3. The calculated heats of mixing for EC/L blends (Fig. 6) are found to be substantially above that figure considered to represent the upper limit of compatibility over most of the composition range, in excellent agreement with the observed behavior. Blends with CAB are suggested to be partially miscible by the same model. Although this is in direct contrast to the observed domain formation by SEM (Fig. 5), limited compatibility is consistent with the conclusion drawn from DSC results. These contradictions may arise from the phase separation of highly ordered liquid crystal regions, a phenomenon inherent to these cellulosic

TABLE 3. Solubility parameter (δ), density (ρ), and monomer unit weight (MW) for blend component polymers.

Polymer	Solubility parameter, δ (cal·cm ⁻³) ^{1/2}	Density, ρ (g·cm ⁻³)	MW (g·mol ⁻¹)
Lignin	11.1	1.24	184
Ethyl cellulose	10.3	1.18	246
Cellulose acetate/butyrate	11.6	1.15	302

derivatives. In the absence of an adequate resolution of this conflict, the nature of the phase separation in the CAB/L blend system remains uncertain.

CONCLUSIONS

Blends of lignin with EC and CAB yielded heterogeneous, two-phase materials over a broad range of compositions according to SEM results. Analysis by DSC and DMTA suggested that the phase separation observed deviates from classical behavior by producing phases with properties that are distinctive from those of the respective pure components and that are sensitive to blend composition. This is supported by: (a) an additional transition in EC blends at temperatures considerably higher than that of either pure component; and (b) by a transition (revealed by DSC) of a second component in CAB blends at a higher temperature than expected. In addition, the discrepancy between observed phase separation and the level of miscibility predicted by simple enthalpic considerations raises some questions concerning the composition and superstructure of the discrete phase formed at low lignin contents in these two binary polymer pairs. More research is needed, however, to establish firmly whether the observed phase separation behavior results from the entropic driving force of liquid crystal mesophase formation or from polymer incompatibility alone.

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